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HIGH OCTANE UNLEADED GASOLINE PRODUCTION

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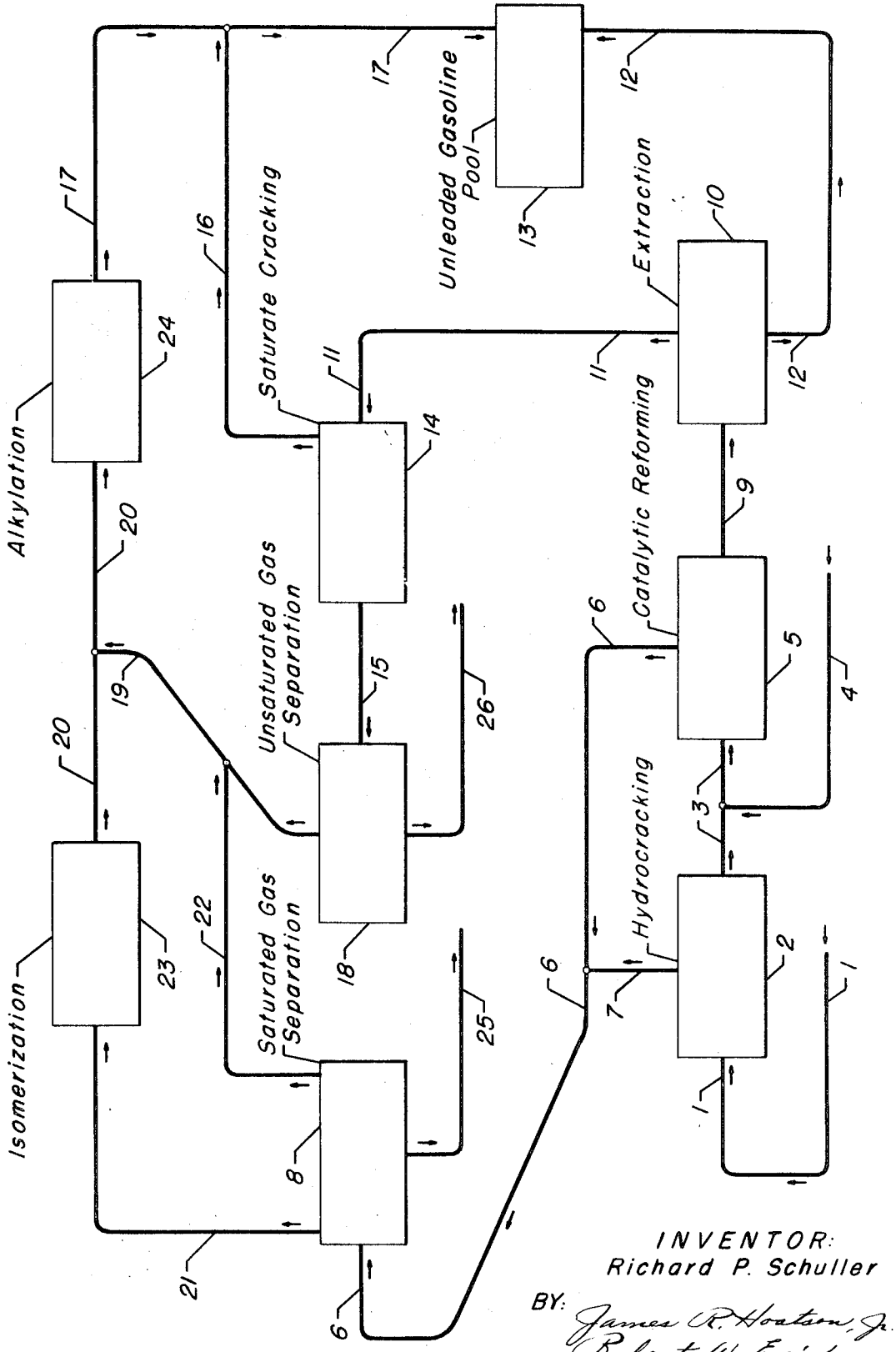

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HIGH OCTANE UNLEADED GASOLINE PRODUCTION

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ABSTRACT OF THE DISCLOSURE

A high octane, unleaded gasoline pool is produced via an integrated refinery operation. The individual processes integrated in combination with each other are hydrocracking, low severity catalytic reforming, saturate cracking and alkylation. Catalytic reforming is effected at low severity conditions to maximize the reaction of naphthene dehydrogenation to produce aromatics which simultaneously inhibiting the dehydrocyclization and cracking of paraffinic hydrocarbons.

APPLICABILITY OF INVENTION

The present invention relates to the conversion of heavy hydrocarbonaceous charge stocks into lower-boiling hydrocarbon products. More specifically, the inventive concept herein described is directed toward an integrated refinery process for producing a high octane, unleaded gasoline pool. Relatively recent investigations into the causes and cures of environmental pollution have indicated that more than about 50.0% of violence to the atmosphere stems from vehicular exhaust consisting primarily of unburned hydrocarbons and carbon monoxide. These investigations have brought about the development of catalytic converters which, when installed in the automotive exhaust system, are capable of converting more than 90.0% of the noxious components into innocuous material prior to the discharge thereof into the atmosphere. In developing these catalytic converters, it was learned that the efficiency of conversion and the stability of the catalytic composite were severely impaired when the exhaust fumes resulted from the combustion of lead-containing motor fuels. Compared to operations of the catalytic converter during the combustion of clear, unleaded gasolines, both the conversion of noxious components and catalyst stability decreased as much as 50.0%. Therefore, it has been recognized throughout the petroleum industry, as well as in the major gasoline-consuming countries, that suitable gasoline must be produced for consumption in internal combustion engines without requiring the addition of lead to increase the octane rating and enhance the anti-knock properties thereof. Also, being recognized is the fact that the unburned hydrocarbons and carbon monoxide are not the only extremely dangerous pollutants being discharged via vehicular exhaust. Japan has experienced an increase in the incidence of lead poisoning, and has enacted legislation to reduce significantly the quantity of lead in motor fuel gasolines.

One natural consequence of the removal of lead from motor fuel gasoline, in addition to many others including the possibility of future engine modifications, resides in the fact that petroleum refining operations must be changed in order to produce voluminous quantities of high octane, unleaded motor fuels. One well known refining process capable of significantly improving the octane rating of gasoline boiling range fractions is the catalytic reforming process. In such a process the primary octane-improving reactions are naphthene dehydrogenation, naphthene dehydroisomerization and paraffin dehydrocyclization. Naphthene dehydrogenation is extremely rapid, and constitutes the principal octane-improving reaction. With respect to five-membered alkyl naphthenes, it is necessary to effect isomerization to produce a six-membered ring naphthene followed by dehydrogenation to an aromatic hydrocarbon. Paraffin aromatization is achieved through dehydrocyclization of straight-chain paraffins having at least six carbon atoms per molecule. The latter reaction is limited in catalytic reforming operations since the aromatic concentration increases through the reforming zone, thereby decreasing the rate of additional dehydrocyclization. Unreacted, relatively low octane paraffins are, therefore, present in the catalytically reformed effluent, and effectively reduce the overall octane rating thereof. At a relatively high severity, the paraffinic hydrocarbons in the reforming zone are subjected to cracking. While this partially increases the octane rating of gasoline boiling range material, substantial quantities of normally gaseous material are produced. In view of the fact that hydrogen is present within the reaction zone, the light gaseous material is substantially completely saturated and comprises principally methane, ethane, propane and butane.

At a relatively low reforming severity, paraffin cracking is decreased with the result that an increased quantity of low octane rating saturates are produced. In order to upgrade the overall quality of the gasoline pool, either the addition of lead becomes necessary, or the low octane rating saturates must be subjected to further processing. As hereinabove set forth, subsequent processing of the saturates for octane rating improvement can be eliminated by increasing the operating severity within the catalytic reforming reaction zone. A high severity operation produces a two-fold effect while increasing the octane rating; first, additional high octane aromatic components are produced and, secondly, the low octane rating components are at least partially eliminated through conversion into either aromatic components, or light normally gaseous hydrocarbons. The results, therefore, include lower liquid yields of gasoline due both to "shrinkage" in molecular size when paraffins and naphthenes are converted to aromatics, and to the production of the aforesaid light gaseous components. These problems are further compounded when the desired end result is the production of a high octane, unleaded gasoline pool. In accordance with the integrated refinery operations constituting the present invention, a low severity catalytic reforming unit is dove-tailed with at least a hydrocracking unit, a saturate cracking unit, and an alkylation unit. As hereinafter indicated, the end result is the production of a high octane, unleaded gasoline pool unaccompanied by substantial liquid yield loss.

The hydrocarbonaceous charge stocks, contemplated for conversion in accordance with the present invention, constitute heavier-than-gasoline hydrocarbon fractions and or distillates. Since "gasoline boiling range hydrocarbons" is intended to connote those hydrocarbons having an initial boiling point of about 100° F. to about 125° F. and an end boiling point from about 400° F. to about 450° F., the contemplated charge stocks will have initial boiling points above about 400° F. The end boiling point of the charge stocks will be about 1050° F., or less, generally considered to be that temperature at which distillation can be effected without incurring thermal cracking. With respect to those hydrocarbonaceous materials containing hydrocarbons which would normally boil above a temperature 1050° F. (considered in the art as "black oils") they are not considered for use until the 1050° F.-plus material, constituting primarily non-distillable asphaltenes, has been removed. Thus, suitable charge stocks intended for conversion through the use of the present process include kerosene fractions, light gas oils boiling up to the temperatures of about 600° F., heavy vacuum or atmospheric gas oils boiling up to a temperature of about 1050° F.

and either intermediate, or overlapping fractions and mixtures thereof. With respect to the gasoline boiling range hydrocarbons, "light naphtha" generally refers to a hydrocarbon mixture concentrated in hydrocarbons having five and six carbons atoms per molecule. Light naphthas can be recovered directly from a crude distillation unit and have an end boiling point in the range of about 175° F. to about 200° F. The heavy naphtha is considered a hydrocarbon mixture having an initial boiling point of about 180° F. and end boiling point of about 400° F. to about 450° F., and includes primarily those hydrocarbons having seven or more carbon atoms per molecule.

OBJECTS AND EMBODIMENTS

A principal object of the present invention is to convert heavier-than-gasoline hydrocarbon distillates into lower-boiling, gasoline boiling range hydrocarbon products. A corollary objective resides in the production of a high octane, unleaded motor fuel gasoline pool.

Another object of my invention is to provide an integrated refinery operation for producing high liquid yields of a high octane, unleaded gasoline pool.

In one embodiment, therefore, my invention affords a process for producing a high octane, unleaded gasoline pool which comprises the steps of: (a) reacting a heavier-than-gasoline charge stock with hydrogen in a catalytic hydrocracking reaction zone, at hydrocracking conditions selected to produce gasoline boiling range hydrocarbon products; (b) separating the resulting hydrocracked product effluent to provide a first substantially saturated vaporous phase and a gasoline boiling range, normally liquid stream; (c) reacting at least a portion of said liquid stream and hydrogen in a low-severity catalytic reforming reaction zone, at reforming conditions selected to convert naphthenic hydrocarbons into aromatic hydrocarbons; (d) separating the resulting reformed product effluent to provide an aromatic concentrate, a saturated normally liquid stream and a second substantially saturated vapor phase; (e) reacting at least a portion of said saturated normally liquid stream in a saturate cracking reaction zone, at cracking conditions selected to produce a cracked gasoline boiling range liquid stream and a substantially unsaturated vaporous phase; (f) reacting at least a portion of said unsaturated vaporous phase with at least a portion of said first and second saturated vaporous phases in an alkylation reaction zone, at alkylating conditions selected to produce an alkylate gasoline boiling range, normally liquid stream; and (g) recovering said aromatic concentrate, said cracked gasoline stream and said alkylate gasoline stream as said high octane, unleaded gasoline pool.

Other embodiments of my invention involve the use of various catalytic composites, operating conditions and processing techniques. In one of such other embodiments, the first and second saturated vaporous phases are separated to provide a butane concentrate, at least a portion of which is reacted with at least a portion of the unsaturated vaporous phase in said alkylation reaction zone. In another such embodiment, the unsaturated vaporous phase is separated to provide a propylene concentrate and a butylene concentrate, the latter being reacted, at least in part, with at least a portion of said first and second vaporous phases in said alkylation reaction zone. In a particularly preferred embodiment, the butane concentrate is separated into a normal butane concentrate and an isobutane concentrate, the former being reacted with hydrogen in an isomerization reaction zone to produce isobutane isomers. These, as well as other objects and embodiments, will become evident from the following more detailed description of the process encompassed by the present inventive concept.

SUMMARY OF THE INVENTION

As hereinbefore set forth, the integrated refinery process of the present invention incorporates a hydrocracking zone, a catalytic reforming zone, a saturate cracking zone and an alkylation reaction zone. Additionally, in other embodiments, the overall process includes an isomerization reaction zone and a solvent extraction zone. In order that a clear understanding of the integrated refinery process of the present invention is obtained, a brief description of the various reaction zones and separation zones, utilized in one or more embodiments of the process is believed to be warranted. In describing each individual zone, one or more references to United States Patents will be made in order that more detail will be readily available where desired. Such references are not intended to be exhaustive or limiting, but merely exemplary.

HYDROCRACKING ZONE

The principal function of the hydrocracking reaction zone is to convert heavier-than-gasoline components into lower boiling, normally liquid products boiling within the desired gasoline boiling range. Depending upon the physical and chemical characteristics of the charge to the hydrocracking zone, the desired reactions will be effected in a single stage or in a multiple-stage system. It is generally conceded, in the hydrocracking art, that the heavier fractions derived from crude oils are contaminated by substantial quantities of both sulfurous and nitrogenous compounds. Therefore, one stage of the overall hydrocracking system will be a hydrorefining reaction zone wherein the sulfurous and nitrogenous compounds are converted into hydrogen sulfide, ammonia and hydrocarbons, the latter being subsequently hydrocracked to form the lower-boiling gasoline components. Exemplary of the hydrocracking process are those schemes and techniques found in U.S. Pats. 3,252,018 (Cl. 208–59), 3,502,572 (Cl. 208–111), and 3,472,758 (Cl. 208–59).

The hydrocracking reaction is generally effected at elevated pressures within the range of about 500 to about 5,000 p.s.i.g., and preferably from 1,500 to about 3,000 p.s.i.g. Circulating hydrogen is admixed with the charge to the hydrocracking reaction zone in an amount of about 3,000 to about 50,000 scf./bbl., and more often in the range of about 5,000 to about 20,000 scf./bbl. The hydrogen and charge stock contacts the catalytic composite, disposed within the hydrocracking reaction zone, at a liquid hourly space velocity of 0.25 to about 5.0, and preferably from about 0.5 to about 3.0. Liquid hourly space velocity is defined as the volumes of fresh feed charge stock per hour, computed at 60° F., per volume of catalyst disposed within the reaction zone. Since the bulk of the reactions being effected are exothermic in nature, an increasing temperature gradient will be experienced as the charge stock traverses the catalyst bed. The maximum catalyst bed temperature is generally maintained in the range of 700° F. to about 900° F., and may be controlled through the use of conventional quench streams which are introduced at intermediate loci of the catalyst bed. Various components of the hydrocracked product effluent which boil above the desired end point of the gasoline product may be recycled to combine with the fresh feed charge stock for further conversion. With respect to the combined liquid feed ratio, defined as total volumes of liquid feed per volume of fresh feed, a range of 1.1 to about 6.0 is not uncommon, although it is generally preferred that the combined feed ratio be in the range of about 1.5 to about 3.0. The selection of any precise combination of operating variables depends on the characteristics of the charge stock, the desired product and the length of time the catalytic composite has been in service.

The hydrocracking catalyst is a composite of a porous carrier material and one or more catalytically active metallic components generally selected from the metals of Groups V–B, VI–B and VIII of the Periodic Table. With respect to the porous carrier material, it may be amorphous, or zeolitic in nature, the latter including well known crystalline aluminosilicates such as faujasite, mordenite, etc. Preferred carrier materials are those compris-

ing alumina and silica, with the latter being in a concentration of about 10.0% to about 90.0% by weight.

The catalytically active metallic components are selected from the group of metals consisting of vanadium, niobium, tantalum, chromium, molybdenum, tungsten, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum. The Group VI–B metals are utilized in a concentration of about 4.0% to about 30.0% by weight, while the Group V–B and iron-group metals are utilized in a lower concentration in the range of about 1.0% to about 10.0% by weight. When the catalytic composite comprises a Group VIII noble metal, particularly platinum and or palladium, the concentration will be in the range of about 0.2 to about 2.0% by weight.

A multiple-stage hydrocracking system is preferred for utilization in the present process. In the first stage, containing a catalytic composite of about 1.8% by weight of nickel and 16.0% by weight of molybdenum, combined with a silica-alumina carrier material containing 37.0% by weight of silica, sulfurous and nitrogenous compounds are removed and some hydrocracking to lower-boiling products is effected. In the second stage, the preferred catalytic composite comprises about 5.0% by weight of nickel combined with a faujasitic carrier material, 90.0% by weight of which is zeolitic.

CATALYTIC REFORMING ZONE

The charge to the catalytic reforming zone is generally derived from at least two sources. The greater proportion of the charge is the gasoline boiling range effluent from the hydrocracking reaction zone. A second source constitutes those naphtha fractions derived from the original crude oil. Since the latter are generally contaminated by sulfurous and nitrogenous compounds, the catalytic reforming reaction zone may have integrated therein a hydrorefining zone which necessarily treats only that portion of the charge derived from the original petroleum crude oil. Catalytic composites, for utilization in the reforming reaction zone, include a refractory inorganic oxide carrier containing a reactive metallic component generally selected from the noble metals of Group VIII. Recent developments in the area of catalytic reforming have indicated that catalyst activity and stability is enhanced through the addition of a Group VII–B or IV–A metal component, particularly rhenium and/or germanium. Suitable porous carrier materials include alumina, crystalline aluminosilicates such as the faujasites, or mordenite, or combinations of alumina with the crystalline aluminosilicates. Generally favored metallic components include ruthenium, rhodium, palladium, osmium, iridium, platinum, rhenium and germanium. These metallic components are employed in concentrations ranging from about 0.01% to about 2.0% by weight. Reforming catalysts may also contain combined halogen selected from the group of fluorine, chlorine, bromine, iodine and mixtures thereof.

Illustrations of catalytic reforming process schemes are found in U.S. Pats. 2,905,620 (Cl. 208–65), 3,000,812 (Cl. 208–138) and 3,296,118 (Cl. 208–100). Effective reforming operating conditions include temperatures within the range of about 800° F. to about 1100° F., and preferably from about 850° F. to about 1050° F. The liquid hourly space velocity is preferably in the range of about 1.0 to about 5.0, although space velocities from about 0.5 to about 15.0 may be employed. The quantity of hydrogen-rich recycle gas in admixture with the hydrocarbon feed stock to the reforming reaction zones, is generally from about 1.0 to about 20.0 moles of hydrogen per mole of hydrocarbon. The reforming reaction zone effluent is introduced into a high pressure separation zone at a temperature of about 60° F. to about 140° F., in order to separate lighter components from heavier, normally liquid components. Since normal reforming operations produce large quantities of hydrogen, a certain amount of the recycle gaseous stream is generally removed from the reforming system by way of pressure control. It is within the scope of the present invention that such excess hydrogen be employed in the hydrogen-consuming hydrocracking reaction zone as make-up hydrogen. Pressures in the range of about 100 to about 1500 p.s.i.g. are suitable for effecting catalytic reforming reactions.

With respect to the catalytic reforming reaction zone utilized in the present combination process, the reactions effected therein are conducted at a relatively low operating severity. To those familiar with the catalytic reforming art, the term "relatively high severity" indicates high temperature or low space velocity, or both high temperature and low space velocity. The most noticeable direct result of high severity operation is found in the octane rating of the normally liquid product effluent. While the reforming zone utilized in the present process does not necessarily upgrade the octane rating of the charge stock to the level ultimately attained with respect to the gasoline pool, the charge stock is substantially improved in octane rating.

In the present specification and accompanying claims, the term "low severity reforming conditions" alludes to a reforming process in which substantial quantities of naphthenes are dehydrogenated to high octane aromatic compounds, while the dehydrocyclization and cracking of paraffinic hydrocarbons are substantially inhibited. Low severity reforming operations may be defined by stating that from about 80.0 to about 100.0 moles of aromatics are produced for every 100.0 moles of naphthenes in the charge stock, while less than about 40.0 moles of aromatics are produced for every 100.0 moles of alkanes. In determining the degree of conversion of naphthenes to aromatics (dehydrogenation) and alkanes to aromatics (dehydrocyclization), it is assumed that a relatively small amount of naphthenes are cracked or otherwise converted to hydrocarbons other than aromatics, and that a major portion of the alkanes which disappear are converted to aromatic hydrocarbons with some naphthenes and higher molecular weight alkanes being converted to low molecular weight normally gaseous components.

SATURATE CRACKING ZONE

As hereinafter set forth in greater detail, the product effluent from the catalytic reforming zone is separated to provide an aromatic concentrate and a saturated liquid stream principally comprising paraffins and naphthenes. The primary function of the saturate cracking zone is to crack the saturated liquid stream. The saturate cracking zone may comprise a catalytic cracking system or a thermal cracking unit. Although the preferred scheme utilizes means for separately recovering an aromatic concentrate from the reforming zone effluent, it is understood that the entire effluent may be introduced into the saturate cracking zone. In either situation, the saurate cracking zone must be capable of selectively cracking the feed stock saturates to lower molecular weight hydrocarbons with the production of dry gases such as methane, ethane, ethylene or acetylene being minimized, whereas the production of propane, propylene, butanes, butylenes and cracked gasoline is maximized. Saturate cracking produces cracked gasoline and valuable light hydrocarbons from the aromatic precursors not converted in the reforming zone, due to the requirement of the low severity conditions, in order to obtain an overall advantage in liquid yield with respect to the high octane gasoline pool.

The materials produced in the saturate cracking zone, in addition to a relatively high octane cracking gasoline, include propane, propylene, normal and isobutane, normal and isobutene, pentanes, and pentenes. These products constitute excellent charge stocks for other processes capable of producing gasoline components such as amines, esters, ethers, ketones, branched-chain paraffins and alcohols. Preferably, the pentanes and heavier hydrocarbons are considered part of cracked gasoline and are in-

troduced as such into the high octane gasoline pool. The remainder of the olefinic portion of the hydrocarbons are especially suited for conversion to the previously described gasoline components, whereas the paraffinic portion of the saturate cracking zone effluent, containing a relatively large quantity of branched-chain isomers, is suited for the production of alkylate gasoline.

Typical, individual gasoline components which can be produced from the light hydrocarbons emanating from the saturate cracking zone include methyl alcohol, ethyl alcohol, isopropyl alcohol, isobutyl alcohol, tertiary butyl alcohol, iso-amyl alcohol, tertiary amyl alcohol, hexanol, isopropylamine, n-butylamine, diethylamine, tri-ethyl amine, methyl acetate, ethyl acetate, isopropyl acetate, isobutyl acetate, propylene oxide, n-propyl ether, isopropyl ether, iso-amyl ether, methyl-ethyl ketone, diethyl ketone, C_3-alkylate and C_4-alkylate. In accordance with the present invention, the butylenes and butanes are utilized as the feed stock to an alkylation reaction zone; the treatment of the propylene concentrate involves either hydrolysis to produce isopropyl alcohol, or alkylation to produce a C_3-alkylate.

The saturate cracking zone requires the use of high activity catalysts and elevated temperature. Preferred reaction temperatures lie within the range of about 850° F. to about 1200° F. An important operating parameter for the selected production of large quantities of propylene and butylene is the contact time between the saturated cracking zone feed and the catalyst contained therein. In fixed-bed cracking, which generally incorporates a once-through operation, the weight ratio of olefins to saturates is almost directly related to the space velocity being utilized with the reaction zone. Increasing the space velocity of the saturated feed increases the amount of olefinic hydrocarbons produced. With respect to fluidized catalytic cracking operations, space velocity is generally measured in terms of weight hourly space velocity, which is defined as the weight of charge per hour per weight of catalyst within the reaction zone. Based upon the raw oil charge, a weight hourly space velocity greater than about 10.0 is preferred, having an upper limit of about 25.0. Where the conversion of the saturate cracking zone feed is relatively low, a portion of the effluent material may be recycled to effect further conversion to propylene and butylenes.

The saturate cracking zone requires a catalyst specifically tailored for the production of the unsaturated light hydrocarbons and cracked gasoline. The catalyst can be selected from a number of known materials including amorphous silica-alumina and zeolitic aluminosilicates, both of which may contain various catalytic components.

Cracking catalysts suitable for use in the saturate cracking zone include silica-alumina, silica-magnesia, silica-zirconia and various crystalline aluminosilicates which are characterized as having high cracking activities. The preferred crystalline aluminosilicate cracking catalyst can be used in admixture with the less active amorphous type, or can be present in substantially pure form. The crystalline aluminosilicate may be naturally-occuring or synthetically-prepared, and includes faujasite, mordenite, type A or type U molecular sieves, etc. Whether the catalyst comprises a crystalline aluminosilicate, or an amorphous material, selected metals may be combined therewith by way of ion-exchange or impregnation. Such combined metals include the rare earth metals and alkaline metals, alkaline-earth metals, Group VIII metals, Group V–B metals, etc. Suitable schemes for effecting the cracking of the saturated liquid stream from the catalytic reforming reaction zone are illustrated in U.S. Pats. 3,161,583 (Cl. 208–164) and 3,206,393 (Cl. 208–164), although specifically directed toward heavier charge stocks.

Although producing larger quantities of lighter hydrocarbons, saturate cracking may be effected thermally. Thermal cracking conditions include pressures ranging from about atmospheric to about 500 p.s.i.g. and temperatures of from about 900° F. to about 1500° F. Preferably, the present combination process utilizes catalytic cracking for the conversion of the saturated liquid stream.

ALKYLATION ZONE

Although the entire normally gaseous portion of the effluent from the saturate cracking zone may be introduced into the alkylation zone, the preferred scheme involves separating these unsaturated gases to provide a butylene concentrate and to recover a propylene concentrate. The latter stream affords a variety of uses including the production of C_3-alkylate or isopropyl alcohol, as hereinbefore set forth, condensation to form isopropylbenzene, polymerization to form tetramer, etc. Preferably, the propylene concentrate is utilized as the feed to a hydrolysis unit for the production of high octane isopropyl alcohol for the introduction into the unleaded gasoline pool, or in combination with the butylene concentrate for alkylate gasoline production. Similarly, although the saturated gaseous phases from both the hydrocracking and catalytic reforming reaction zones may be introduced directly into the alkylation zone, in admixture with the unsaturated gaseous phase, a preferred scheme involves separating the saturated gaseous phases to produce a butane concentrate and to recover propane. Probably the most economic use of the latter is as a blending component for liquefied petroleum gas (LPG). In another preferred embodiment, the butane concentrate, provided by the saturated gas separation, is further separated into a normal butane concentrate and an isobutane concentrate, the latter being admixed with the butylenes and propylene for conversion in the alkylation reaction zone. The normal butane concentrate is subjected to isomerization in order to produce additional quantities of isobutane.

Separation of the unsaturated gaseous phase and the saturated gaseous phases may be accomplished in any suitable manner known to the art. However, it is preferred that the saturated gaseous phase be separated in a zone distinct from the zone utilized to separate the unsaturated gaseous phases. Techniques suitable for effecting the separation of the gaseous phases utilize distillation, adsorption, stripping, cryogenic separations, diffusion, etc.

The alkylation reaction zone may be any acidic catalyst reaction system such as a hydrogen fluoride-catalyzed system, or one which utilizes a boron halide in a fixed-bed reaction system. Hydrogen fluoride alkylation is particularly preferred, and may be conducted substantially as set forth in U.S. Pat. No. 3,249,650 (Cl. 260–683.48). Briefly, the alkylation reaction when conducted in the presence of hydrogen fluoride catalyst, is such that the catalyst to hydrocarbon volume ratio within the alkylation reaction zone is from about 0.5 to about 2.5. Ordinarily, anhydrous hydrogen fluoride will be charged to the alkylation system as fresh catalyst; however, it is possible to utilize hydrogen fluoride containing as much as 10.0% water or more. Excessive dilution with water is generally to be avoided since it tends to reduce the alkylating activity of the catalyst and further introduces corrosion problems. In order to reduce the tendency of the olefinic portion of the charge stock to undergo polymerization prior to alkylation, the molar proportion of isoparaffins to olefinic hydrocarbons in an alkylation reactor is desirably maintained at a value greater than 1.0, and preferably from about 3.0 to about 15.0. Alkylation reaction conditions, as catalyzed by hydrogen fluoride, include a temperature of from 0° to about 200° F., and preferably from about 30° F. to about 125° F. The pressure maintained within the alkylation system is ordinarily at a level sufficient to maintain the hydrocarbons and catalyst in a substantially liquid phase; that is, from about atmospheric to about 40 atmospheres. The contact time within the alkylation reaction zone is conveniently expressed in terms of space-time, being defined as the volume of catalyst within the reactor contact zone divided by the volume rate per minute of hydrocarbon reactants charged to the zone.

Usually the space-time will be less than 30 minutes and preferably less than about 15 minutes.

When the alkylation reaction of the combination process of the present invention is effected as a fixed-bed unit utilizing a boron halide catalyst, such as boron trifluoride, the operating conditions will be substantially those as set forth in U.S. Pat. No. 3,200,165 (Cl. 260–671), notwithstanding that this patent teaches an alkylation-transalkylation process for the production of ethylbenzene. The amount of boron trifluoride is relatively small, and generally not more than about 1.0 gram of boron trifluoride per gram mole of the olefinic hydrocarbon. The boron trifluoride alkylation reaction zone is of the conventional fixed-bed type, and contains a boron trifluoride-modified inorganic oxide selected from diverse inorganic oxides including alumina, silica, boria, oxides of phosphorous, titania, zirconia, zinc oxide, mixtures of two or more, etc. The operating conditions may be varied over a relatively wide range, the precise selection generally being dependent upon the character of both the olefinic hydrocarbon as well as the paraffinic hydrocarbon. In any event, the alkylation reaction may be effected at a temperature of about 0° to about 250° C., and under a pressure of from about 15 to about 200 atmospheres, or more. The pressure is usually selected to maintain the reaction mixture substantially in the liquid phase at the selected operating temperature. The liquid hourly space velocity through the alkylation reaction zone may likewise be varied over a relatively wide range of from about 0.1 to about 20.0, or more. In addition to the foregoing, suitable alkylation reaction schemes are indicated in U.S. Pats. 2,832,812 (Cl. 260–683.42) and 2,818,415 (Cl. 260–683.4).

ISOMERIZATION ZONE

As hereinbefore set forth, a preferred scheme involves separating a saturated gaseous phase from both the hydrocracking and catalytic reforming reaction zone to provide a butane concentrate. In addition to the butane concentrate, the saturated gas separation zone permits recovery of a hydrogen-rich stream which may be recycled to the hydrocracking and reforming zones, a methane-ethane concentrate which is utilizable as fuel gas and a propane concentrate for use as LPG. With respect to the butane concentrate, although it may be introduced directly into the alkylation reaction zone, a preferred scheme involves further separation to concentrate the isobutane for alkylation purposes, and the normal butanes which serve as the charge stock to the isomerization zone. As indicated in U.S. Pat. No. 2,900,425 (Cl. 260–666), the isomerization process is effected in a fixed-bed system utilizing a catalytic composite of a refractory inorganic oxide carrier material, a Group VIII noble metal component and a metal halide of the Friedel-Crafts type. As previously indicated, the refractory oxide carrier material may be selected from the group of metallic oxides including alumina, silica, titania, zirconia, alumina-boria, silica-zirconia, and various naturally-occurring refractory oxides. Of these, a synthetically-prepared gamma alumina is preferred. The Group VIII noble metal is generally present in an amount of about 0.01% to about 2.0% by weight, and may be one or more metals selected from the group of ruthenium, rhodium, osmium, iridium, and particularly platinum or palladium. Suitable metal halides of the Friedel-Crafts type include aluminum chloride, aluminum bromide, ferric chloride, ferric bromide, zinc chloride, beryllium chloride, gallium chloride, titanium tetrachloride, zirconium chloride, stannic chloride, etc. The quantity of the Friedel-Crafts metal halide will be within the range of about 2.0% to about 25.0% by weight.

The isomerization reaction is preferably effected in a hydrogen atmosphere utilizing sufficient hydrogen so that the hydrogen to hydrocarbon mole ratio of the reaction zone feed will be within the range of from about 0.25 to about 10.0. Operating conditions will further include temperatures ranging from about 100° C. to about 300° C., although temperatures within the more limited range of about 150° C. to about 275° C. will generally be utilized. The pressure under which the reaction zone is maintained will range from about 50 to about 1,500 p.s.i.g. A fixed-bed type process is preferred, with the butane and hydrogen feed passing through the catalyst in downward flow. The reaction products are separated from the hydrogen, which is recycled. and subjected to fractionation and separation to produce the desired reaction product. Recovered starting material is also recycled so that the overall process yield is high. Liquid hourly space velocities will be maintained within the range of about 0.25 to about 10.0, and preferably within the range of about 0.5 to about 5.0. Another suitable isomerization process, for the production of isobutane, is found in U.S. Pat. No. 2,924,628 (Cl. 260–666).

AROMATIC EXTRACTION ZONE

As hereinbefore set forth, the catalytic reforming zone is maintained under relatively low severity operating conditions in order to produce a product effluent rich in aromatic hydrocarbons and normally liquid saturates including paraffins and cyclo-paraffins. The saturated material is converted into a cracked gasoline in the saturate cracking zone. Although the entire liquid portion of the reforming zone effluent, including the aromatics, may be introduced into the saturate cracking zone, a preferred technique involves separating the reformed product effluent to recover the aromatics contained therein. Although any separation scheme may be utilized, a greater degree of efficiency is achieved through the use of a solvent extraction zone. Solvent extraction to produce an aromatic concentrate and a paraffinic raffinate is a well known technique which is thoroughly described in the literature. Suitable techniques involve the operations illustrated in U.S. Pats. Nos. 2,730,558 (Cl. 260–674) and 3,361,664 (Cl. 208–313).

The solvent extraction process utilizes a solvent having a greater selectivity and solvency for the aromatic components than for the paraffinic components contained in the reformed product effluent. Selective solvents may be selected from a wide variety of normally liquid organic compounds of generally polar character; that is, compounds containing a polar radical. The selective solvent is one which boils at a temperature above the boiling point of the hydrocarbon mixture at the ambient extraction pressure. Illustrative specific organic compounds, useful as selective solvents in extraction processes for the recovery of aromatic hydrocarbons include the alcohols, such as methanol, ethanol and higher homologous monohydric alcohols; the glycols, such as ethylene glycol, propylene glycol, butylene glycol, tetra-ethylene glycol, glycerol, etc; the glycol ethers, such as di-ethylene glycol, di-propylene glycol, di-methyl ether of ethylene glycol, tri-ethylene glycol, tri-propylene, etc.; other organic solvents well known in the art for extraction of hydrocarbon components from mixtures thereof with other hydrocarbons may be employed. A particularly preferred class of solvents are those characterized as the sulfolane-type. Thus, as indicated in U.S. Pat. No. 3,470,087 (Cl. 208–321), the preferred solvent is one having the 5-membered ring, one atom of which is sulfur, the other four being carbon and having two oxygen atoms bonded to the sulfur atom. In addition to sulfolane, the preferred class includes the sulfolenes such as 2-sulfolene and 3-sulfolene.

The aromatic selectivity of the preferred solvents can be further enhanced by the addition of water. This increases the selectivity of the solvent phase for aromatic hydrocarbons over non-aromatic hydrocarbons without reducing substantially the solubility of the solvent phase for aromatic hydrocarbons. The solvent composition contains from about 0.5% to about 20.0% by weight of water, and preferably from about 2.0% to about 15.0%, depending on the particular solvent and the process conditions under which the extraction, extractive distillation and solvent recovery zones are operated.

In general solvent extraction is conducted at elevated temperatures and pressures selected to maintain the charge stock and solvent in the liquid phase. Suitable temperatures are within the range of from 80° F. to about 400° F. and preferably from about 150° F. to about 300° F. Operating pressures include super-atmospheric pressures up to about 400 p.s.i.g., and preferably from about 50 p.s.i.g. to about 150 p.s.i.g.

Typical extractive distillation zone pressures are from atmospheric pressure up to about 100 p.s.i.g., although the pressure at the top of the distillation zone will generally be maintained in the range of about 1 p.s.i.g. to about 20 p.s.i.g. The reboiler temperature is dependent upon the composition of the feed stock and the selected solvent, although temperatures of from about 275° F. to 360° F. appear to yield satisfactory results. The solvent recovery system is operated at low pressures and sufficiently high temperatures to drive the aromatic hydrocarbons overhead, thus producing a lean solvent bottoms stream. Preferably, the top of the solvent recovery zone is maintained at pressures of from about 100 to about 400 millimeters of mercury absolute. These low pressures must be used since the reboiler temperature should be maintained below about 370° F. to avoid thermal decomposition of the organic solvent.

DESCRIPTION OF DRAWING

A preferred embodiment of the present invention is illustrated in the accompanying drawing. The illustration is presented by way of a block-type flow diagram, in which each block represents one particular step or stage of the process. Miscellaneous appurtenances, not believed necessary for a clear understanding of the present combination process, have been eliminated from the drawing. The use of details such as pumps, compressors, instrumentation and controls, heat-recovery circuits, miscellaneous valving, start-up lines and similar hardware, etc., is well within the purview of one skilled in the art. Similarly, with respect to the flow of materials throughout the system, only those major streams required to illustrate the interconnection and interaction of the various zones are presented. Thus, various recycle lines, vent gas streams, etc., have been eliminated also.

The drawing will be described in conjunction with a commercially-scaled unit designed to process 100,000 bbl./day of a full boiling range crude oil having a gravity of about 39.4° API and containing about 0.3% by weight of sulfurous compounds, calculated as elemental sulfur. From an external source, normal butane, in an amount of 5,000 bbl./day, and isobutane in an amount of about 2,000 bbl./day is provided. Not illustrated in the drawing is the initial separation of the crude oil by way of distillation techniques and vacuum separation which results in 5,400 bbl./day of an asphaltic residuum, 5.372 bbl./day of a low sulfur, No. 6 bunker fuel, 2,772 bbl./day of a No. 2 fuel oil and 3,100 bbl./day of a range oil. Of the remaining 83,356 bbl./day, 53,119 constitutes the charge stock to the hydrocracking zone of the present process, and 30,237 bbl./day constitutes the crude oil distillation overhead. This overhead stream contains those hydrocarbons boiling below a temperature of about 400° F., and is combined with the 7,000 bbl./day of external normal butane and isobutane.

The overhead stream from the crude distillation unit is initially introduced into a debutanizer from which a C_4-minus stream, containing a minor quantity of pentanes, is removed in an amount of about 10,606 bbl./day. A bottoms stream, principally C_5-400° F. hydrocarbons, is passed into a splitter in order to recover 21,993 bbl./day of a heptane-400° F. naphtha fraction to serve as a portion of the charge to the catalytic reforming zone. The C_5/C_6 concentrate, in an amount of 4,638 bbl./day, forms part of the feed to the saturate cracking zone. Since the intended charge to the reforming reaction zone contains detrimental quantities of sulfurous and nitrogenous compounds, it is first introduced into a naphtha hydrorefining reaction zone wherein the contaminating influences are converted into hydrogen sulfide, ammonia and hydrocarbons. The intended object of this commercially-scaled unit is to produce an unleaded gasoline pool having an octane rating (Research Method) of at least 95.0.

Referring now to the accompanying drawing, the 53,119 bbl./day of 400° F.-plus material from the crude distillation column is introduced into hydrocracking zone **2** by way of line **1**. In the present illustration, hydrocracking zone **2** is a two-stage system functioning in series flow, in the first stage of which sulfurous and nitrogenous compounds are converted into hydrogen sulfide and hydrocarbons, and some conversion into lower-boiling hydrocarbons is effected. The second stage involves additional hydrocracking into gasoline boiling range materials. The catalytic composite disposed in the first stage of hydrocracking zone **2** is a composite of 1.8% by weight of nickel and 16.0% by weight of molybdenum combined with an amorphous alumina-silica carrier material comprising 37.0% by weight of silica. The charge is admixed with about 10,000 scf./bbl. of hydrogen, and passes into the reaction zone at a temperature of about 650° F., a pressure of about 2,100 p.s.i.g. and a liquid hourly space velocity of about 1.63. An increasing temperature gradient of 100° F. is experienced, and the product effluent is withdrawn at a temperature of about 750° F. Following its use as a heat-exchange medium, to reduce the temperature to about 700° F., the product effluent, without intermediate separation, passes into the second stage which contains a catalytic composite of 5.0% by weight of nickel combined with a crystalline aluminosilicate carrier material, about 93.0% by weight of which is zeolitic and constitutes faujasite. The operating pressure is about 2,050 p.s.i.g., the fresh feed liquid hourly space velocity is about 0.90 and about 4,000 scf./bbl. (on fresh feed) of hydrogen is utilized as a quench stream to maintain the increasing temperature gradient at a level of about 20° F.

The effluent is separated, following use as a heat-exchange medium and further cooling to a temperature of about 100° F., in a high-pressure (2,000 p.s.i.g.) separator to provide a hydrogen-rich gaseous phase and a principally liquid phase. The gaseous phase may be subjected to one or more treatments to remove hydrogen sulfide and light, saturated hydrocarbons to increase the hydrogen concentration prior to recycle thereof to the first stage of the system. The principally liquid phase is separated into various component streams, and hydrocarbonaceous material boiling above 400° F. is recycled to combine with the first stage effluent, thereby providing a combined liquid feed ratio to the second stage of about 1.60. Overall hydrogen consumption is 3.48% by weight, or 2,117 scf./bbl., based upon fresh feed to the first stage. The final product distribution and yield is presented in Table I.

TABLE I

Hydrocracking Yields and Distribution

Component	Weight percent	Volume percent
Ammonia	0.18	
Hydrogen sulfide	1.06	
Methane	0.32	
Ethane	0.46	
Propane	3.19	
Isobutane		13.85
n-Butane		5.94
Pentane/hexane		30.22
Heptane-400° F.		77.20

The butanes and lighter hydrocarbons (exclusive of hydrogen sulfide and ammonia) are withdrawn through line **7** and passed by way of line **6** into saturated gas separation zone **8**. The heptane-400° F. fraction passes by way of line **3** into catalytic reforming zone **5** in ad-

mixture with the hydrorefined straight-run naphtha stream from the crude distillation column in line **4**; the total liquid naphtha feed to reforming zone **5** is 61,106 bbl./day, of which 41,007 bbl./day is the hydrocracked naphtha from line **3**. The pentane/hexane hydrocracked light naphtha concentrate, in an amount of 16,052 bbl./day may be included as part of the liquid feed to reforming zone **5**. However, since it has a research octane rating (RON) of about 84.7, a preferred technique, not illustrated in the accompanying drawing, recovers this stream as a separate product from hydrocracking zone **2**, and incorporates the same into unleaded gasoline pool **13**.

Catalytic reforming zone **5**, in the present illustration, is designed to produce maximum quantities of a normally liquid reformate product having an RON of about 92.0. This product stream is intended to include pentanes and higher-boiling hydrocarbons in the gasoline boiling range. The reforming reaction zone **5** contains a catalytic composite of alumina, 0.375% by weight of platinum, about 0.25% by weight of germanium and about 0.85% chloride, calculated as the elements. The operating conditions imposed upon the catalytic reforming zone include a pressure of 250 p.s.i.g., a liquid hourly space velocity of about 2.3, an average catalyst bed temperature of about 940° F. to about 970° F. and a hydrogen to hydrocarbon mole ratio of about 5.0:1.0.

The reformed product effluent is separated within reforming zone **5** into a hydrogen-rich recycle stream, a butane-minus gaseous phase in line **6** and a pentane-containing, normally liquid stream in line **9**. Catalytic reforming is a hydrogen-producing process, and excess hydrogen over that required to satisfy the mole ratio of 5.0:1.0 may be employed to supplant that hydrogen consumed within hydrocracking reaction zone **2**. The saturated gaseous phase in line **6** is admixed with the saturated gaseous phase in line **7**, the mixture continuing through line **6** into saturated gas separation zone **8**. The 10,606 bbl./day of C_4-minus concentrate, including the 7,000 bbl./day of outside butanes, is also introduced into saturated gas separation zone **8**. The pentane-plus portion of the reformed product effluent preferably passes through line **9**, in an amount of about 50,494 bbl./day, into extraction zone **10**.

As hereinbefore set forth, extraction zone **10** is not considered essential to the present combinative process, but constitutes one preferred embodiment. The normally liquid, catalytically reformed product effluent is introduced into the lower portion of an extraction column countercurrently to a lean solvent stream introduced into an upper portion of said column, the mole ratio of solvent to hydrocarbon being about 3.2:1.0. The selected solvent is sulfolane, and the column conditions are a top pressure of about 15 p.s.i.g. and a reboiler temperature of about 320° F. A saturate-rich raffinate stream is withdrawn as an overhead product while the rich solvent bottoms stream is introduced into an extractive distillation zone. Additional raffinate is withdrawn as an overhead stream, combined with the saturate-rich raffinate from the extraction column, and passed from extraction zone **10**, via line **11** into saturate cracking zone **14**; the saturated raffinate is in an amount of about 23,484 bbl./day. Rich solvent is introduced into a solvent recovery zone functioning at sufficiently low pressures and high temperatures to drive aromatic hydrocarbons overhead while producing a lean solvent bottoms stream for recycle to the extraction column. The aromatic concentrate, in an amount of about 27,010 bbl./day, is withdrawn from extraction zone **10** through line **12** and introduced thereby into unleaded gasoline pool **13**. With respect to the raffinate stream in line **11**, beneficial results are obtained, with respect to subsequent saturate cracking, when the stream is substantially sulfolane-free. One possible technique for removing solvent from the saturate-rich raffinate is that disclosed in U.S. Pat. No. 3,470,087 (Cl. 208–321).

Including the 4,638 bbl./day of C_5/C_6 light naphtha from the crude distillation column, the total feed to saturate cracking zone **14** is 28,122 bbl./day. The cracking of the saturated raffinate is effected in a fluid catalytic cracking system utilizing a cracking catalyst containing 10.0% by weight of faujasite in a silica matrix and about 2.7% by weight of alumina. The system functions much the same as the well known fluid catalytic cracking process which is exemplified in U.S. Pats. 3,161,583 (Cl. 208–164) and 3,206,393 (Cl. 208–164). The saturate cracking is effected at a reactor temperature of about 1050° F., the regenerator temperature being about 1250° F., and with a catalyst to charge stock weight ratio of 15.6:1.0. Since there is no liquid recycle to the reactor, the combined liquid feed ratio is 1.0. The results of the saturate cracking operation are presented in the following Table II:

TABLE II

Saturate cracking yields and distribution

Component	Weight percent	Volume percent
Hydrogen	0.9	
Methane	5.3	
Ethane	2.6	
Ethylene	6.8	
Propane	2.2	3.2
Propylene	21.3	29.8
Isobutane	4.6	6.0
n-Butane	0.9	1.1
Butylenes	15.4	18.4
Pentane-400° F.	35.0	33.3
Coke	5.0	

The pentane-400° F. gasoline fraction, in an amount of 9,247 bbl./day, is removed from saturate cracking zone **14** through line **16**, and, via line **17**, is sent to the unleaded gasoline pool **13**. An unsaturated gaseous phase, comprising butylenes and lighter components, being about 60.0% by weight of the feed to saturate cracking zone **14**, passes by way of line **15** into unsaturated gas separation zone **18**. With respect to this gaseous phase, the hydrogen, methane, ethane and ethylene may be first separated in the saturate cracking zone so that the feed to gas separation zone **18** is primarily a C_3/C_4-concentrate rich in propylene and butylenes. The particular means selected for separating the gaseous phase into the desired component streams is not pertinent to my invention, and any techniques described in the art, and easily recognized by those having expertise therein, may be utilized.

In the commercial design being used to illustrate this embodiment, the quantity of propylene is such that about 500 bbl./day are withdrawn from the process through line **26**, for use, in this instance, as a raw material for the production of isopropyl benzene. The remainder of the propylene is withdrawn through line **19** in admixture with the butanes and butylenes, and introduced via line **20** into alkylation zone **24**. In this fashion, both C_3-alkylate and C_4-alklylate gasolines are produced.

Saturated gas separation zone **8** serves to concentrate the C_4-hydrocarbons contained in (1) the gaseous phase from the crude distillation column, (2) the saturated vaporous phase in line **7** from hydrocracking reaction zone **2** and (3) the saturated vaporous phase in line **6** from catalytic reforming zone **5**. A propane concentrate is removed from the process system by way of line **25**, in an amount of about 57,234 lbs./hr., or about 7,725 bb./day. Propane may be dehydrogenated to propylene to produce additional C_3-alkylate gasoline, tetramer or isopropyl benzene, or utilized as a component of LPG.

Although the total C_4-hydrocarbon stream may be sent directly to alkylation reaction zone **24**, with subsequent recycle of unreacted butanes to isomerization zone **23**, a preferred technique involves further separation into an isobutane concentrate and a normal butane stream. The former is removed from separation zone **8** through line **22**, and is passed via lines **19** and **20** into alkylation reaction zone **24**; the latter, in line **21**, forms part of the feed to isomerization reaction zone **23**, the remainder of the feed being recycled unreacted butanes from the alkyla-

tion reaction zone **24** (the recycle line is not illustrated in the drawing).

Isomerization reaction zone **23** utilizes a fixed-bed reaction zone containing a catalytic composite of alumina, about 19.0% by weight of aluminum chloride, and 0.375% by weight of platinum, calculated as the elemental metal. The reaction zone is maintained under a pressure of about 300 p.s.i.g., a temperature of about 300° F. and a hydrogen to hydrocarbon molal ratio of about 1.0:1.0. The reactants traverse the catalyst bed at a liquid hourly space velocity of about 1.0. Following separation of gaseous material, the butane portion of the product effluent is passed into alkylation reaction zone **24** by way of line **20**, in admixture with the butane/butylene concentrate in line **19**.

Alkylation reaction zone **24** is a hydrofluoric acid system which produces about 23,341 bbl./day of alkylate gasoline, of which about 9,381 bbl./day is C_4-alkylate. The reaction time, utilizing a pumped acid settler reactor, is about nine minutes and the acid/hydrocarbon volume ratio is about 1.5:1.0. The alkylation reactions are effected at a temperature of about 100° F. Following separation of unreacted butanes, which are recycled to isomerization reaction zone **23**, and a minor quantity of cracked products, the alkylate gasoline passes through line **17** into unleaded gasoline pool **13**.

A summary of the results of the foregoing combinative process is presented in the following Table III:

TABLE III.—UNLEADED GASOLINE POOL

Component stream	Quantity, bbl./day	RON	RVP [1]
Light hydrocracked naphtha	16,052	84.7	10.6
Cracked gasoline	9,364	94.0	6.7
C_3-alkylate	13,981	92.0	1.9
C_4-alkylate	9,381	97.0	1.6
Aromatic gasoline	27,010	115.0	0.8
Isopentane	1,451	93.0	20.4
n-Pentane	962	61.7	15.6
Isobutane	838	102.1	85.0
n-Butane	6,989	94.0	65.0
Total	86,028	98.6	10.1

[1] The vapor pressure specification of the entire gasoline pool requires addition of butanes to reach a level of 10.0.

From Table III, it is noted that 86,028 bbl./day of a 98.6 RON (research octane rating) unleaded gasoline pool is produced by the present combination process. Based upon 100,000 bbl./day of total crude oil charge and 7,000 bbl./day of outside butanes (107,000 bbl./day total), the volumetric yield of gasoline is 80.4%. Economic studies indicate that the incremental cost of producing this unleaded gasoline pool, with respect to the commercial unit being considered, is only $0.268/bbl., or 0.638 cents/gallon.

The foregoing demonstrates the method by which the present invention is effected and the benefits afforded through the utilization thereof.

I claim as my invention:

1. A process for producing a high octane, unleaded gasoline pool which comprises the steps of:

(a) reacting a heavier-than-gasoline charge stock with hydrogen in a catalytic hydrocracking reaction zone, at hydrocracking conditions selected to produce gasoline boiling range hydrocarbon products;

(b) separating the resulting hydrocracked product effluent to provide a first substantially saturated vaporous phase and a gasoline boiling range, normally liquid stream;

(c) reacting at least a portion of said liquid stream and hydrogen in a low-severity catalytic reforming reaction zone, at reforming conditions selected to convert naphthenic hydrocarbons into aromatic hydrocarbons;

(d) separating the resulting reformed product effluent to provide an aromatic concentrate, a saturated normally liquid stream and a second substantially saturated vaporous phase;

(e) reacting at least a portion of said saturated normally liquid stream in a saturate cracking reaction zone, at cracking conditions selected to produce a cracked gasoline boiling range liquid stream and a substantially unsaturated vaporous phase;

(f) reacting at least a portion of said unsaturated vaporous phase with at least a portion of said first and second saturated vaporous phases in an alkylation reaction zone, at alkylating conditions selected to produce an alkylate gasoline boiling range, normally liquid stream; and,

(g) recovering said aromatic concentrate, said cracked gasoline stream and said alkylate gasoline stream as said high octane, unleaded gasoline pool.

2. The process of claim **1** further characterized in that said first and second saturated vaporous phases are separated to provide a butane concentrate, at least a portion of which is reacted with at least a portion of said unsaturated vaporous phase in said alkylation reaction zone.

3. The process of claim **2** further characterized in that said butane concentrate is separated to provide a normal butane concentrate and an isobutane concentrate, and said butane concentrate is reacted with hydrogen in a hydroisomerization reaction zone, at isomerizing conditions selected to product isobutane isomers.

4. The process of claim **3** further characterized in that said isobutane isomers and said isobutane concentrate are reacted in said alkylation zone with at least a portion said unsaturated vaporous phase.

5. The process of claim **1** further characterized in that said unsaturated vaporous phase is separated to provide a propylene concentrate and a butylene concentrate, the latter being reacted, at least in part, with at least a portion of said first and second vaporous phases in said alkylation reaction zone.

6. The process of claim **4** further characterized in that the alkylation reaction zone effluent is separated to recover unreacted butanes, said butanes being recycled to said hydroisomerization reaction zone.

7. The process of claim **1** further characterized in that said saturate cracking reaction zone is a catalytic cracking zone.

8. The process of claim **1** further characterized in that said saturate cracking reaction zone is a thermal cracking reaction zone.

9. The process of claim **5** further characterized in that said propylene concentrate is converted to an alcohol in a hydrolysis reaction zone.

10. The process of claim **1** further characterized in that said reformed product effluent is separated in a solvent extraction zone.

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